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Particle Size Distribution of Nitrate Aerosols in the Los Angeles Air Basin

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ABSTRACT

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SECTION 1

INTRODUCTION

Previous investigators (1-6) have shown that particulate nitrate compounds, derived from nitric oxide emissions, make up a significant fraction of the total atmospheric loading in the Los Angeles air basin. In order to obtain accurate size distribution data for nitrates it is necessary to use a technique which is capable of measuring small quantities of nitrate. Wet chemical techniques including extraction, colorimetric methods, and use of the nitrate specific electrode, often require large sample sizes and excessive sample handling which increase the risk of contamination and restrict the lower limit of detectability. An aerosol vaporization technique is described here which measures nitrate at nanogram levels directly from the collection substrate. The vaporization procedure and apparatus are similar to the method described by Roberts and Friedlander (7) for sulfate. A brief description follows as the details may be found in that publication.

SECTION 2

APPARATUS

Stainless steel strips one inch long upon which aerosol has been deposited, are mounted across two tungsten posts in a small glass cell. A nitrogen flow of 1.2 liters per minute passes into the cell where it picks up vaporized products resulting from a rapid heating of the steel strip. The strip, acting as a resistance, is heated by the discharge of a capacitor (190,000 MFD at 11.6 volts). The vaporized sample is then carried into a nitrogen oxide detector.

The detector used is a chemiluminescent NO/NO_2 analyzer (Thermoelectron Corp. Model 14B) which is capable of measuring NO or NO_2 concentrations up to 10 ppm. The NO determination is accomplished by a gas phase titration of the NO with ozone. The intensity of the light emitted by the chemiluminescent $NO-O_3$ reaction has been shown to vary linearly with NO concentration over many orders of magnitude (8,9). The instrument is equipped with a molybdenum catalyst operated at 450°C which, by reducing NO_2 to NO, allows measurement of NO_2. Other converters (10) are used to convert organic nitrates such as nitrosoamines to NO so that these may also be measured. The effectiveness and sensitivity of the chemiluminescent technique has been demonstrated by its use in conjunction with a gas chromatograph. N-nitroso compounds at the sub-ppb level have been quantitatively identified in air, water and foodstuffs (11).

The chemiluminescent analyzer is calibrated by using an NO calibration gas produced by a dilution system (Kin-Tek Precision Calibration System Model 570). A flow of nitric oxide in a nitrogen diluent is produced in this system by a permeation membrane which produces calibration gases having concentrations of a few tenths of a ppm.

The vaporization of nitrate results in the formation of NO_x; less than 1% of the nitrate is converted to NO_2. However, in order to be certain that all of the nitrogen oxides are measured the catalyst is used and all oxides of nitrogen are monitored. The vaporization may be carried out in air; tests with zero air yield the same results. The chemiluminescent analyzer responds rapidly to the NO pulse sent from the vaporization apparatus. The response time of the analyzer is short enough to permit quantitative NO detection. A scale setting on the analyzer must be chosen so that the amplitude of the output signal (ppm NO_x) will lie between 5 and 95 percent of full scale in order to assure accuracy and avoid saturation of the instrument. Generally a full scale setting of 2 ppm is employed which provides a maximum input pulse of 250 ng of nitrate. At this setting all output signals have accurately measurable traces. The quantity of nitrate vaporized is related to the output trace by means of the equation:

$$\text{Mass } NO_3 = \frac{(\text{Trace area})(\text{MW of } NO_3)(\text{Flow in l/min})(\text{Atmospheric P})}{(K \text{ in counts/ppm-min})(R)(T \text{ in } {}^{0}K)(10^6 \text{ppm})} \quad (1)$$

where the area is given in counts; K, a constant determined from the scale chosen for the integrator; R, the gas constant in liter-atm/mole-^{0}K; the atmospheric pressure in atm. An electronic integrator (Varian Aerograph Model 477 Electronic Integrator) determines the area under each pulse . The input flow rate is held constant by the detector.

SECTION 3

ANALYSIS AND CALIBRATION

Stainless steel strips were baked in a furnace for 1 hour at 900°C. A sample of 23 strips was examined for background levels. It was found that the strips contained 1.7 ng of N (standard deviation 0.63 ng), equivalently 5.6 ng NO_2 or 7.5 ng NO_3. Furthermore, it was discovered that after the strips were blanked by capacitor discharge, adsorption occurred upon exposure to ambient air. About 0.5 ng of NO_x, calculated as N, is adsorbed in 1 minute. It was determined that a limit of approximately 2 ng of NO_x, as N, is reached in a few hours. This falls within the range of the average strip background and suggests that the adsorbed species is responsible for the background. No correlation was found between the ambient NO_x levels and the quantity of gas adsorbed. It is believed that the history of the strip surface is the more important factor in explaining background levels. Because of adsorption the lower limit of quantitative nitrate analysis is about 25 ng of NO_3. A non-adsorbing surface would increase the sensitivity of the method.

Standard solutions are placed on preflashed strips using a 1 microliter syringe, and are allowed to dry in the nitrogen stream. Solutions of NH_4NO_3, $NaNO_3$, $Pb(NO_3)_2$, $(NH_4)_2SO_4$ and HNO_3 were prepared using doubly distilled water and predried salts. Figure 1 shows the measured NO, calculated as nitrate, vs. the quantity of nitrate placed on the strip. By considering the ammonium nitrogen to have a nitrate equivalent on the abscissa $(NH_4)_2SO_4$ is included to show that ammonium ion is not detected. The low levels observed for $(NH_4)_2SO_4$ are due to impurities in the standards. The standard deviation (excluding HNO_3 and $(NH_4)_2SO_4$) is 15%, predominantly arising from the preparation of the standards rather than from the technique itself. The HNO_3 recovery is poor since its low boiling point and high

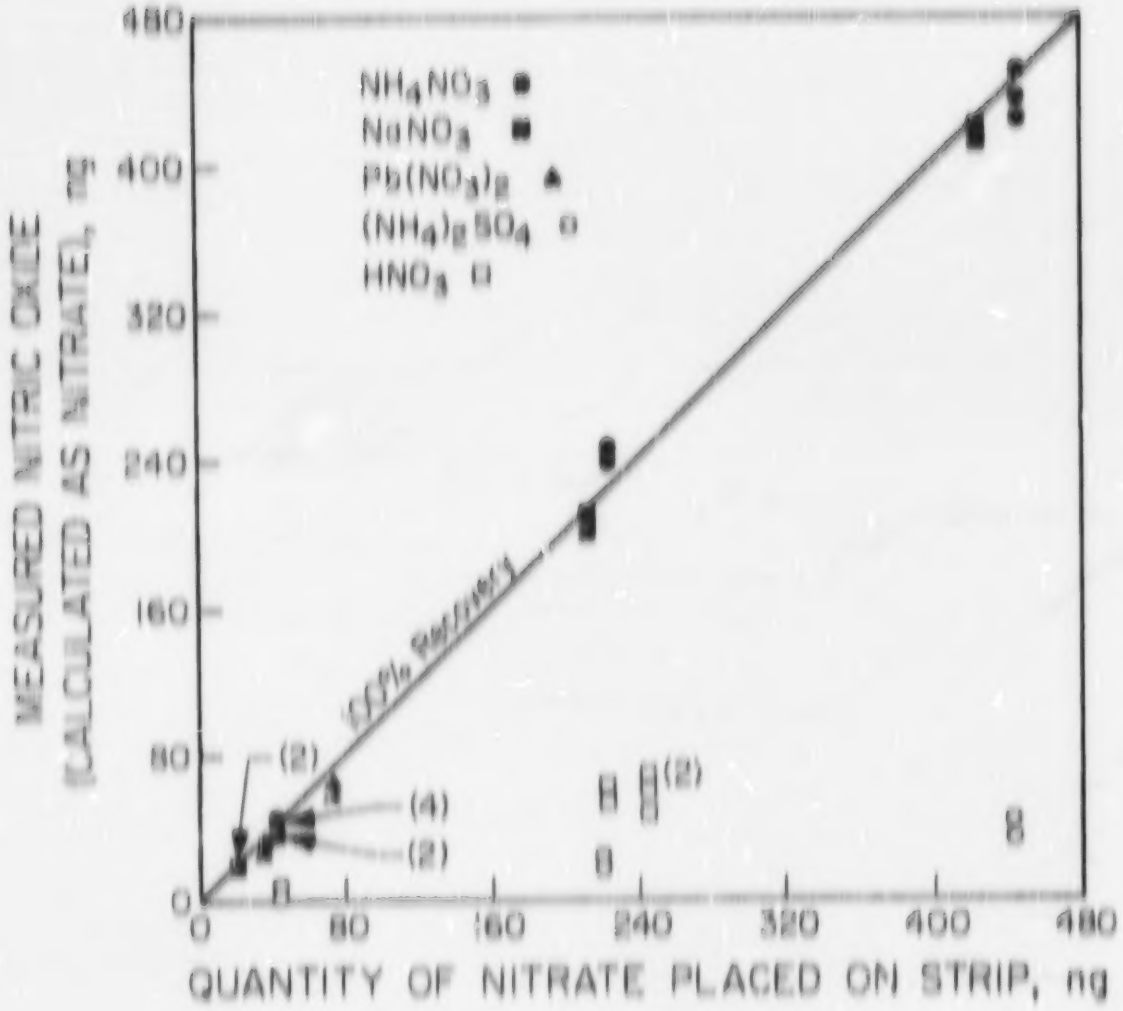

Figure 1. Recovery of nitrate for different compounds. The numbers to right of a data point indicate the number of trials it represents. For $(NH_4)_2SO_4$, the nitrate equivalent to the ammonia content is indicated on the abscissa.

volatility promote its evaporation from the strip. When using large aliquots of HNO_3 the detector actually responds to a pulse of NO_x prior to the heating of the strip. All of the salts investigated have vaporization or decomposition points under 500°C, far below the 1200°C temperatures to which the strips are exposed. Our studies show that under or over baking the strips by as little as half an hour sharply reduces the recovery of nitrate after vaporization.

The stainless steel strips are mounted in a single jet, 8 stage, low pressure impactor which is capable of size fractionating aerosols in the submicron range; lower diameter cutoffs, in microns, are 4, 2, 1, 0.5, 0.25, 0.11, 0.05, 0.03 (12) Lundgren (2) reported that the aerosol collected on the stages of an impactor may be 20-30% less than that collected by a total filter. This is especially true when solid particulate matter as opposed to watery aerosol is collected. An attempt was made to determine exactly how much nitrate was passing through the impactor by placing a glass fiber filter after the last stage of the impactor. Since good quantitative nitrate recovery was possible by sandwiching a piece of the filter (0.25 cm in diameter) between 2 strips and heating at 25 volts, it seemed possible to measure any nitrates not collected in the impactor. This approach was abandoned as the nitrate levels on the after filter could not be measured with sufficient accuracy to permit quantitative analysis. The levels were almost the same as that of the filter background due to the low volume of gas passing through the filter. In addition, the standard deviation for a given filter was about 25% of the total nitrate present and tended to obscure any results. It was then assumed that bounce off occurred and we chose to find a suitable coating for the strips.

The best coating would be a compound which is sticky, nonvolatile, nitrate free, and does not combine with the highly reactive NO that is evolved during the sample heating. Various substances were tried including glycerol, silicone grease, mineral oil and vaseline. Vaseline was the most suitable although the blank levels were not always negligible. The vaseline is applied with a cotton swab in a very thin layer. The nitrate level on the coated strip is 12 ng NO_3, standard

deviation is 5 ng. Studies done with ambient aerosol indicate that there is a 25-65 percent increase in the total nitrate collected when using the coated strips as compared to the uncoated ones. It was possible to compare total nitrate collected by the impactor with that collected by a glass fiber filter (Gelman type AE). In all cases the level of nitrate on the after filter was not measureable, due to the aforementioned difficulties. Table I shows the data for 3 comparisons. The flow through the impactor is 1 liter per minute; that through the filter is 44 liters per minute. Within experimental error the nitrate levels obtained by both methods were identical.

TABLE 1. COMPARISON OF IMPACTOR AND FILTER COLLECTION OF NITRATE

Nitrate collected by impactor, $\mu g/m^3$	Nitrate collected by filter, $\mu g/m^3$*	Duration of sample, minutes
14.0	13.6	60
6.42	7.3	80
47.8	41.1	25

*Standard deviation is 25%

SECTION 4

AMBIENT NITRATE MEASUREMENTS

Measurements of aerosol nitrate were made at three locations in the South Coast air basin; Pasadena, Hermosa Beach (30 miles SW of Pasadena), and Chino (an agricultural area 30 miles SE of Pasadena). The 8 stage, low pressure impactor sampled at a flow rate of 1 liter per minute. Six samples were obtained over the period 7 AM to 7 PM with each sample being 1-2 hours in duration. The strips were analyzed the same day.

The data for the three locations for each run are shown in Figure 2. It is seen that in midmorning, regardless of location, there is a significant quantity of particulate matter in the submicron range. This is also apparent in the late afternoon data of Chino and Pasadena, suggesting that this size range may well be associated with auto exhaust.

An average diurnal nitrate size distribution for each location was obtained by time averaging the nitrate levels present on like stages of the impactor. The distributions are shown in Figure 3. The Pasadena distribution is bimodal; peaks exist in the two size ranges .05-1 μm and 2-8 μm (8 μm is an arbitrary upper cutoff). The Chino experiment, near an ammonia rich cattle feed area, possesses a significant peak in the submicron range although the distribution appears to be weakly bimodal. In the coastal area the predominant size range for nitrates is in the 2-8 μm region. Pasadena may be thought of as possessing aerosol characteristics of both coastal and agricultural regions.

It is of interest to compare these results with those of other investigators. Lundgren (2) reported that on days of heavy smog in the eastern region of the basin (Riverside), a large amount of crystalline, hygroscopic particulate matter was present in the .5-1 μm range. X-ray diffraction identified it as NH_4NO_3. Infrared spectra studies by Grosjean (1) show that NH_4NO_3 comprises 95% of the total

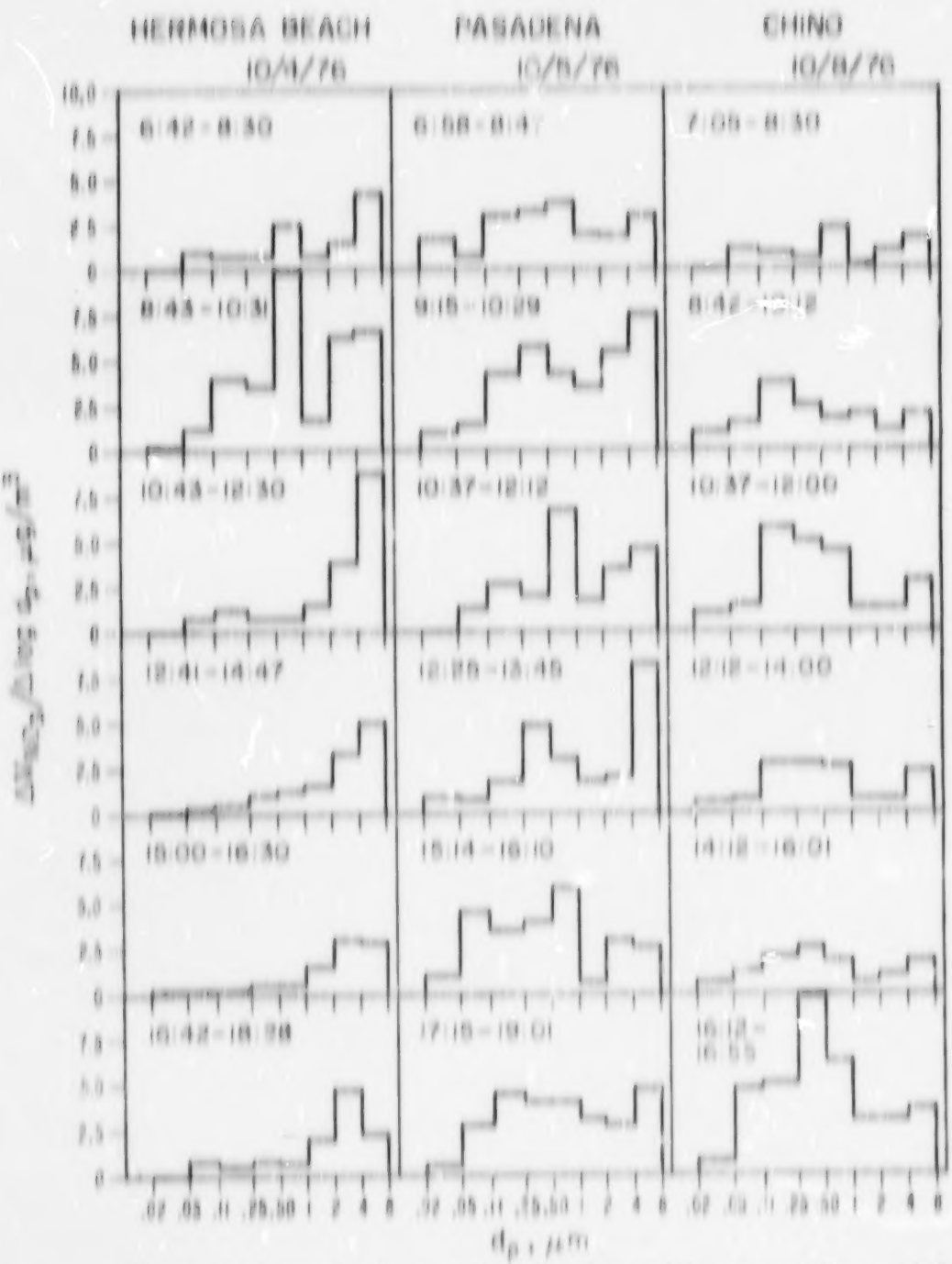

Figure 2. Aerosol nitrate distributions with respect to particle size for different locations at various times of day.

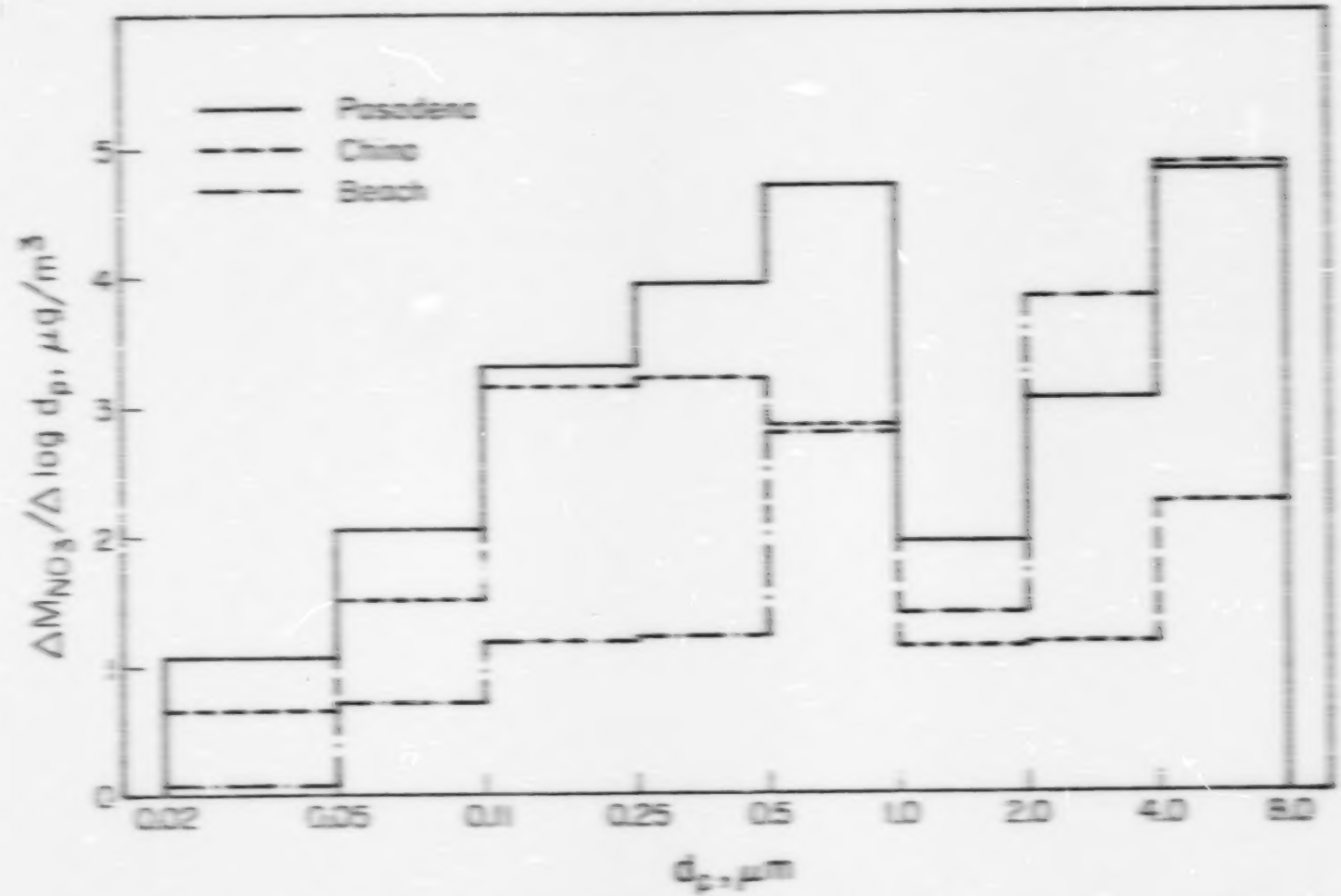

Figure 1. The average diurnal distribution for aerosol nitrate with respect to particle size for different locations.

nitrate aerosol. In an investigation by O'Brien (6), inorganic nitrate and other particulate pollutants were measured in a number of California locations. It was found that inorganic nitrate (NH_4NO_3 and $NaNO_3$) of a secondary or photochemical origin contributed about 10% of the mass loading in the South Coast air basin. The prevalent form of nitrate in the basin was NH_4NO_3; the NH_4^+ concentration was the highest in the Los Angeles air basin compared to other California locations. The study also showed that the coastal Santa Barbara sample contained 16 % inorganic nitrate while the NH_4^+ concentration was essentially zero. This indicates that the reaction of NO_2 with NaCl is of importance in coastal areas. The mechanism has been postulated to be (13):

$$3NO_2 + H_2O = 2HNO_3 + NO \qquad (2)$$

$$HNO_3 + NaCl = NaNO_3 + HCl \qquad (3)$$

The data indicate that the Pasadena aerosol consists of both small NH_4NO_3 and larger $NaNO_3$ particles. The data from each location were grouped into 2 categories: particles with diameter greater than 2.0 μm and those with diameter less than 2.0 μm. The percentage of the total nitrate existing as small particles for each location was plotted as a function of time (Figure 4a). The total nitrate as a function of time is included (Figure 4b). The data for Pasadena and Chino show that the percentage of nitrate as small particles is reasonably constant over the day. In the case of the beach it can be noted that the small particle fraction is significant in the morning, while the larger marine aerosol dominates later in the day.

Nitrogen gas-particle distribution factors were calculated for Pasadena experiments. The distribution factor f_N is defined as:

$$f_N = \frac{NO_3^-}{NO_x + NO_3^-} \qquad (4)$$

where NO_3^- = particulate nitrate concentration, as NO_2, $\mu g/m^3$ and NO_x = gas phase concentration as NO_2, converted from ppm to $\mu g/m^3$, averaged over the sampling period. The data are presented in Table 2. The distribution factors are in the same range reported by Grosjean. It

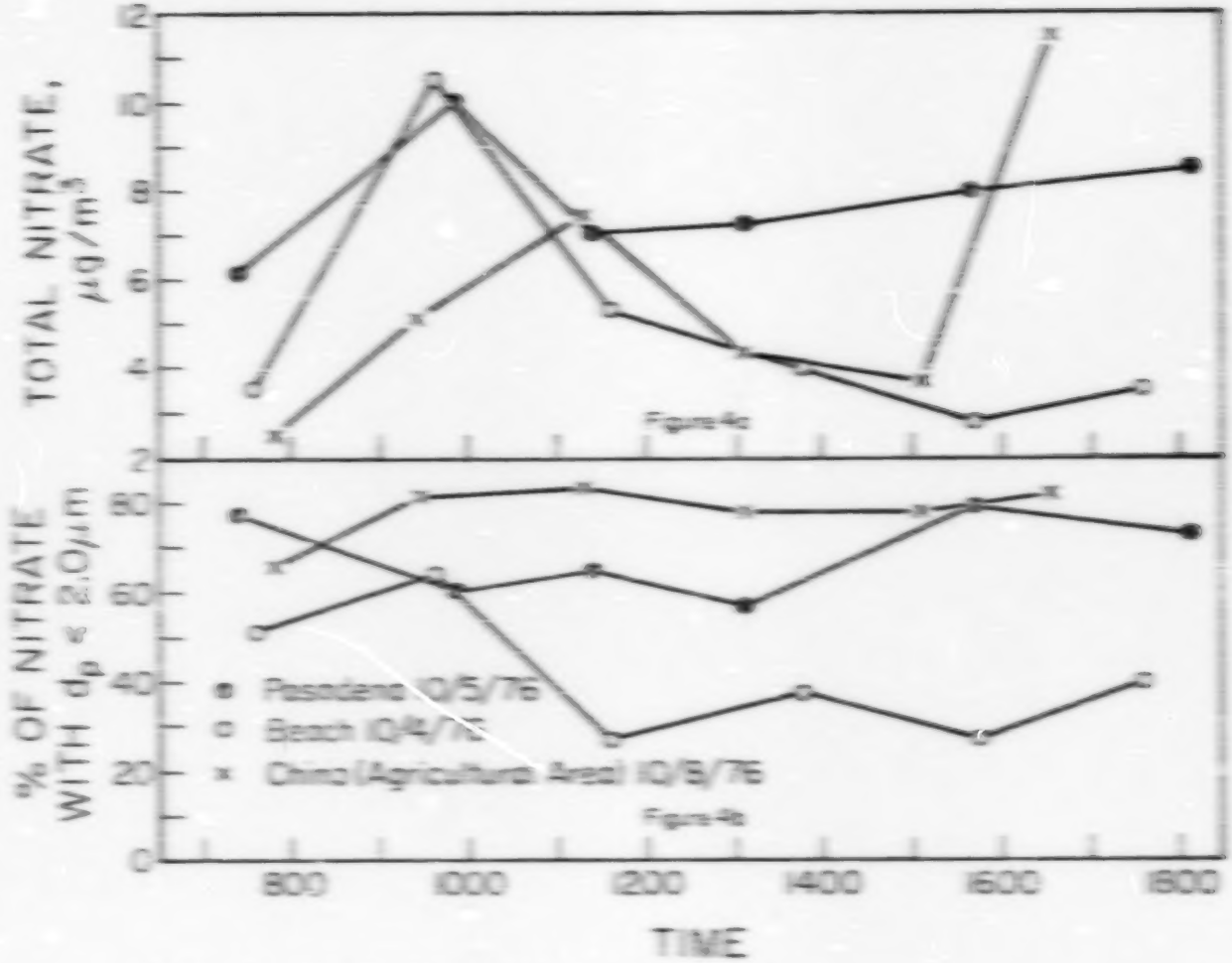

Figure 4a. Total nitrate as a function of time.
Figure 4b. The diurnal variation of the sub-2.0 μ nitrate fraction.

TABLE 2. NITRIC OXIDE CONCENTRATIONS AND DESTRUCTION FACTORS FOR PASADENA

TIME*	NO_x (ppm)	NO_x (as NO_2) $\mu g/m^3$	NO_3^- (as NO_2) $\mu g/m^3$	f_N
Pasadena 9/30/76				
9:57	.047	52.0	2.80	.041
11:00	.031	33.2	3.95	.067
12:44	.028	30.0	2.80	.056
14:15	.027	28.9	2.39	.044
15:48	.031	33.2	1.81	.028
17:15	.043	46.0	2.37	.025
Pasadena 10/5/76				
7:23	.150	161	4.57	.028
9:52	.075	80.2	7.38	.084
11:24	.031	33.2	5.22	.136
13:05	.020	21.4	5.37	.200
15:42	.032	34.2	5.91	.147
18:06	.020	21.4	6.31	.228

*The time shown is the midpoint of the sample interval

would be very interesting to monitor NO_2 levels at the beach and agricultural areas to determine if the abundance of stabilizing cations (NH_4^+, Na^+) actually increases the distribution factor.

It is of interest to look at the amounts of $NaNO_3$ which would correspond to the ambient levels of Na. Sodium was measured in the ACHEX experiment (14) and the level was determined to be roughly 0.7 $\mu g/m^3$. This corresponds to a level of 1.89 $\mu g/m^3$ of NO_3^-. If one time averages the levels of particles with diameter greater than 2.0 μm for each of the locations it is found that beach nitrate is 2.6 $\mu g/m^3$, Pasadena 2.4 $\mu g/m^3$, and Chino 1.0 $\mu g/m^3$. This would be consistent with the hypothesis that the concentration of Na should decrease as one gets farther inland, with decreasing levels of large particles. It is seen that by a rough approximation the concentration of large particles in Pasadena is consistent with the concentration predicted by ambient Na levels. One might expect that other anions such as SO_4^{-2} and Cl^- would form stable sodium salts also.

Visibility degradation has been correlated with high aerosol mass concentration. As a result of the ACHEX study it was determined that nitrate is a less efficient light scatterer than sulfate. Presumably this is due to the fact that all of the sulfate exists in a highly efficient light scattering range (.1-1.0 μm) whereas only part of the nitrate is found in this range.

SECTION 5

CONCLUSIONS

A method has been developed which permits the fractionation and analysis of inorganic nitrate aerosols with a minimum of sample handling. Although the vaporization and chemiluminescent detection of nitrate is accurate, the vaseline coating restricts the lower limit of nitrate analysis to 25 ng, which may correspond to a relative error of as much as 25%.

Nitrate size distributions vary dramatically with location. Marine aerosol, present in the greater than 2.0 μm fraction, decreases in concentration as one gets farther inland. $NaNO_3$ is the principal nitrate species in afternoon coastal aerosol. In the inland agricultural area of China, the level of marine aerosol is low. While ammonium nitrate aerosol in the sub-2.0 μm fraction is the predominant nitrate species in China, it exerts only a small perturbation on the coastal nitrate size distribution. The mixture of aerosols from both coastal and agricultural regions is exhibited in the bimodal nitrate size distribution of Pasadena.

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APPENDIX A

Nitrate and NO_x Chemistry

The NO_x ($NO + NO_2$) that usually enters the urban atmosphere is primarily NO which is formed during combustion. Although some NO_2 may be formed via the overall reaction:

$$2NO + O_2 = 2NO_2 \qquad (1)$$

most of it is produced by the reaction of NO with ozone, the latter formed in the atmosphere by the action of sunlight on O_2. NO_2 is also dissociated by sunlight. The predominant processes for nitrate chemistry are the following reactions:

$$NO_2 + h\nu = NO + O \qquad (2)$$
$$O + O_2 + M = O_3 + M \qquad (3)$$
$$O_3 + NO = NO_2 + O_2 \qquad (4)$$

Other reactions produce intermediate species and have been shown to have some significance (15). These reactions are:

$$O_3 + NO_2 = NO_3 + O_2 \qquad (5)$$
$$NO_3 + NO_2 = N_2O_5 \qquad (6)$$
$$N_2O_5 + H_2O = 2HNO_3 \qquad (7)$$

However, these reactions alone do not explain the typical diurnal pattern observed for these species. Whereas one would expect the concentration of NO_2 to be diminished as sunlight irradiation continued, with a steady level of O_3 produced rapidly, actually substantial amounts of O_3 are produced and increase dramatically. Referring to Figure 5, the ozone peak corresponds to the peak in solar intensity. NO concentration correlates with the morning rush hour traffic as one would expect.

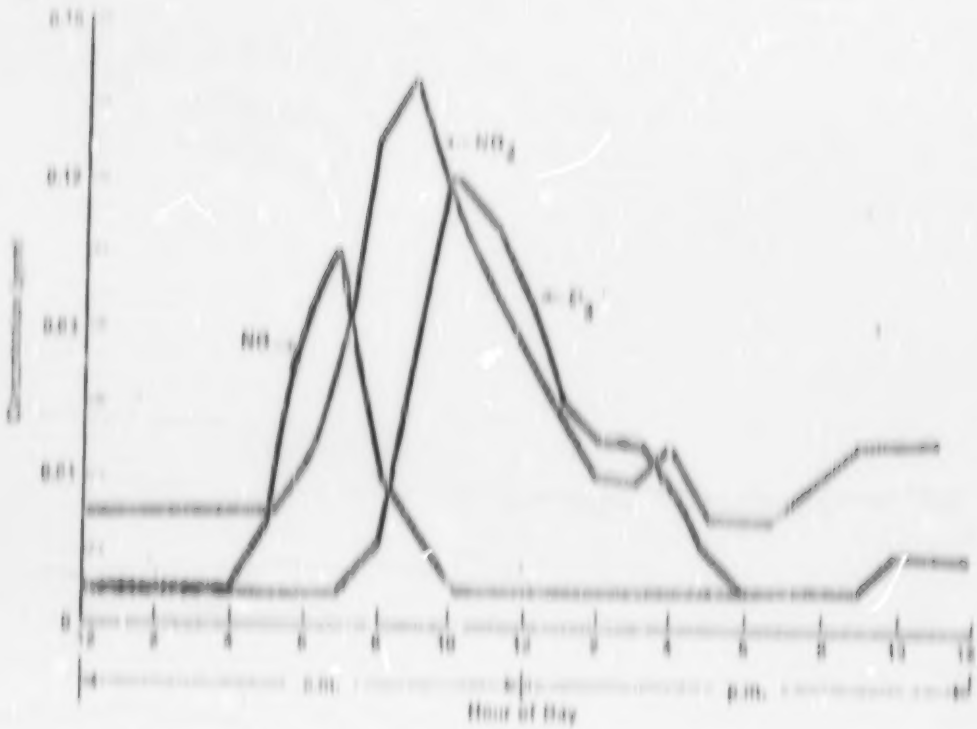

Figure 5. Typical diurnal profile of Los Angeles smog.

In order for the ozone level to peak, it cannot be used in oxidizing NO to NO_2. A number of researchers have demonstrated (17, 18) that other species can contribute to the oxidation of NO without the consumption of ozone. One such mechanism involves CO. Nitrous acid, formed in the overall reaction:

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 \qquad (8)$$

photolyzes according to:

$$HNO_2 + h\nu \rightarrow NO + OH \qquad (9)$$

and generates a minor source of the free hydroxyl radical. These hydroxyl radicals react with CO, also a combustion product, to yield CO_2 plus a hydrogen free radical, which reacts with O_2 to give the hydroperoxyl radical, HO_2 (16):

$$OH + CO \rightarrow H + CO_2 \qquad (\text{—})$$
$$H + O_2 + M \rightarrow HO_2 + M \qquad (11)$$
$$HO_2 + NO \rightarrow NO_2 + OH \qquad (12)$$
$$OH + CO \rightarrow H + CO_2 \text{ etc.} \qquad (10)$$

Thus, NO_2 is formed without the consumption of ozone. However, this mechanism does not entirely account for the levels or the rates required to explain the patterns observed in the atmosphere. Various organics introduced into the atmosphere during incomplete combustion of fuel generate the HO_2 radical. Olefins are particularly susceptible to attack by ozone and generate many acylperoxy ($RC(=O)O_2$) or alkylperoxy (RO_2) compounds which are capable of acting as oxidizing agents. Peroxyacetylnitrate (PAN) is a common, stable compound which is formed by:

$$CH_3\text{-}C(=O)\text{-}O\text{-}O + NO_2 \rightarrow CH_3\text{-}C(=O)\text{-}O\text{-}O\text{-}NO_2 \qquad (13)$$

This reaction tends to lower the amount of free NO_2 available for generating inorganic nitrates such as NH_4NO_3 and $NaNO_3$.

The relationship between the nitric oxides and particulate nitrate is not well understood. It is assumed that nitric acid formed in reaction (7) reacts with NH_3 for example, yielding NH_4NO_3. The NH_3

may well be solvated prior to the reaction. NH_3 is introduced into the atmosphere by means of a variety of sources including auto exhaust, industrial exhaust, and evaporation from cattle feed lots. Urban ammonia concentrations have been estimated to be up to 0.2 ppm with an average of 0.02 ppm (15). As previously stated, NH_4NO_3 has been determined to be the major particulate nitrate in the Los Angeles area, accounting for up to 95% of all particulate nitrates.

The study by Novakov,et al. (3) is interesting because pyridine and amine nitrogen were detected primarily in the small, .6 to 2.0 μm diameter size range, whereas nitrates were found to be present in only the 2 to 6 μm range. The amine and pyridine nitrogen are known to be contained in gasoline additives.

Generally, researchers in the Los Angeles area, including the eastern part of the basin, report concentrations of nitrate between 5 and 50 $\mu g/m^3$, with an average of about 7 $\mu g/m^3$. The levels in San Francisco, for example, are lower, the average being 2.8 $\mu g/m^3$ over a 5 year period (4). There is still considerable question as to the size range of nitrate aerosol, which has been the subject of this paper.

APPENDIX B

Techniques and Apparatus

VAPORIZATION APPARATUS

Figure 6 shows a diagram of the glass vaporization cell and the associated circuitry. It is important to keep the stainless steel washers free of dirt; they are periodically cleaned with fine sandpaper. The strips, .8 in. x .21 in., are cut from .001 inch thick stainless steel shim stock, type 302 full hard. Holes are punched in the strips so as to fit the tungsten posts. The strips are wiped clean with a lint free cloth and heated in a furnace for 1 hour at 900°C. Low nitrate background levels are produced in this way.

CHEMILUMINESCENT DETECTOR

The chemiluminescent NO_x analyzer is only one of the many methods available used to measure NO and NO_2 concentrations. It is however, the easiest to use and is the most accurate since it does not require the dissolution of ambient gases into a solvent with the attendant wet chemical methods. The analysis is performed entirely in the gas phase. The method takes advantage of the gas phase chemiluminescent reaction between NO and O_3; the mechanism has been shown to be:

$$NO + O_3 \xrightarrow{k_1} NO_2 + O_2 \qquad (14)$$

$$NO + O_3 \xrightarrow{k_2} NO_2^* + O_2 \qquad (15)$$

$$NO_2^* \xrightarrow{k_3} NO_2 + h\nu \qquad (16)$$

$$NO_2^* + M \xrightarrow{k_4} NO_2 + M \qquad (17)$$

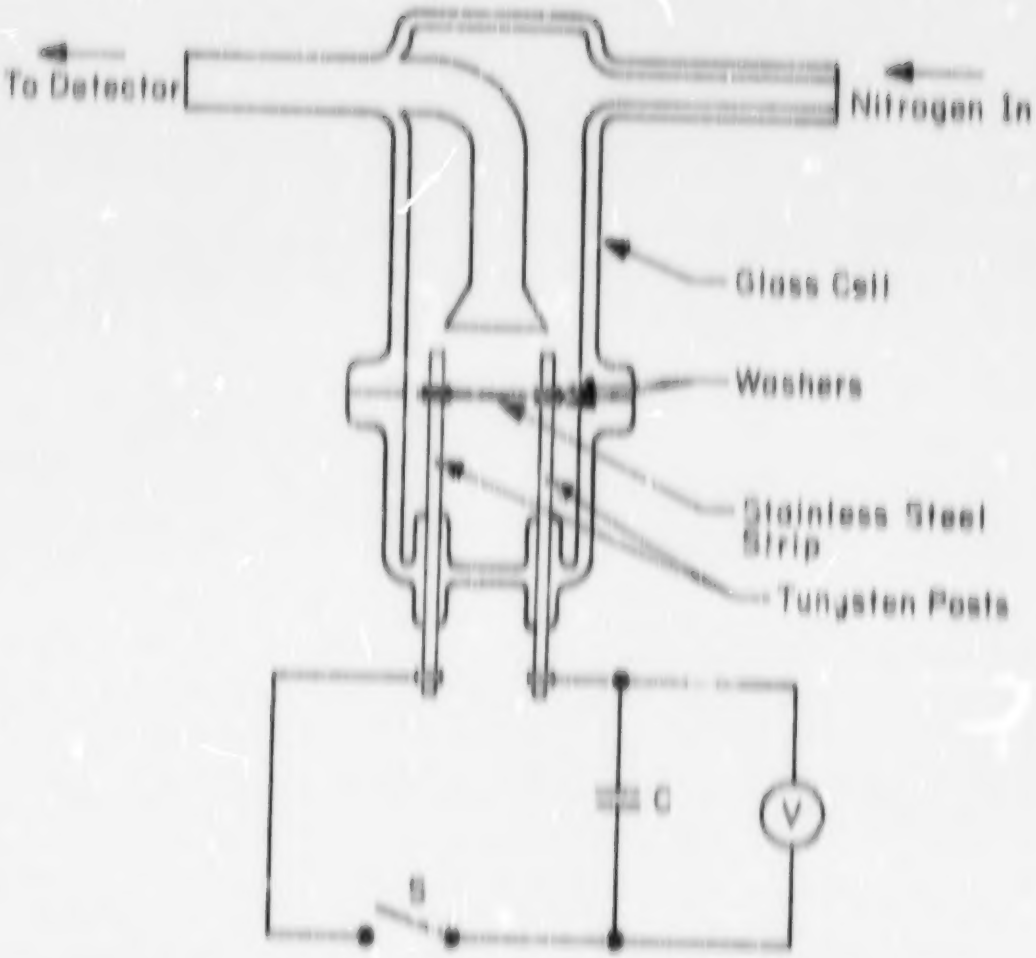

Figure 6. Aerosol vaporization apparatus and associated circuitry.

where M is any gaseous species present and NO_2^* represents an electronically excited NO_2 molecule. The activation energies for reactions 14 and 15, are 2.4 and 4.2 kcal/mole, respectively. Approximately 10% of the reacting NO follows reaction 15 (20). The reaction between NO and O_3 is bimolecular and the energy of the excited state is about 40 kcal/mole. The intensity can be related to the concentration of the reactant species as follows:

We assume that NO_2^* is in steady state, and making that approximation we have the following: (18)

$$\frac{d(NO_2^*)}{dt} = k_2 (NO)(O_3) - k_3 (NO_2^*) - k_4 (NO_2^*)(M) = 0$$

$$(NO_2^*) = \frac{k_2(NO)(O_3)}{k_4(M) + k_3} \qquad (19)$$

In designing the system the concentration of M is kept as low as possible by using a reaction chamber at low pressure; k_3 becomes the more significant factor, yielding:

$$\text{Intensity } I = K(NO_2^*) = \frac{k_2(NO)(O_3)}{k_3} \qquad (20)$$

or,

$$I = \frac{I_0 (NO)(O_3)}{k_3} \qquad (21)$$

Fontijn (8) was the first to look into the possible use of this reaction as a method for measuring the amount of NO present in the atmosphere. Certainly the predominant reason for his investigation lies in the specificity of the wavelength of the light emitted in the reaction. With the proper selection of filters only the desired reaction will be monitored. Fontijn's system basically consisted of a one liter glass reaction chamber into which the ozone (from an O_3 generator) and NO are separately added. A vacuum pump kept the reaction chamber pressure at one torr. A photomultiplier tube with an appropriate filter was used to monitor the reaction. One of the most significant results of this work was to show that the method is

highly linear; that is the light intensity varies linearly with NO concentration over the range 4 ppb to 100 ppm. This represents the range investigated rather than the limits of reaction linearity. Also of great importance was the fact that the introduction of gases found in the polluted atmosphere (at higher than normal concentrations) had no significant effect on the reaction. Gases tried were NO_2-9 ppm, CO_2-300 ppm, CO-300 ppm, C_2H_4-5 ppm, NH_3-9 ppm, SO_2-25%, H_2O-25% saturation.

About a year after Fontijn's paper, Stuhl and Niki (9) at Ford essentially duplicated Fontijn's work although they made some variations in the experimental setup. One of their important observations was that at sufficiently high partial pressures of NO and O_3, the NO_2^* intensity became less susceptible to small pressure fluctuations. They believed that this was the effect of balancing the rate of formation and deactivation of NO_2^*.

Another possible reaction to use for the measurement of NO is:

$$NO + O + M = NO_2^* + M \qquad (22)$$

$$NO_2^* = NO_2 + h\nu \qquad .4\mu m<\lambda<1.4\mu m \qquad (23)$$

However, in this case an interfering reaction is:

$$NO_2 + O = NO + O_2 \qquad (24)$$

The above reaction mechanism is suitable for measuring NO plus NO_2.

Many significant improvements have been made in the technique. Hedgeson, et al., have developed a method for measuring NO in ambient concentrations with a reactor operated at atmospheric pressure. This might me of great importance in designing portable equipment since a vacuum pump would not be necessary. Recent application of the technique has been made to the measurement of NO_2. The earliest work on NO_2 conversion to NO with application to chemiluminescence was by Stusby (10), who observed quantitative conversion of NO_2 to NO by means of a stainless steel tube heated to 600°C.

$$2NO_2 \xrightarrow[\text{catalyst, heat}]{\text{stainless steel}} 2NO + O_2 \qquad (25)$$

It is known that the rate of dissociation of NO_2 to NO increases with

increasing temperature. Dissociation begins at 150°C and is 100% completely dissociated at 620°C. The rate of NO oxidation to NO_2 decreases with increasing temperature. In the case that CO and hydrocarbon levels are much greater than the concentration of oxygen, NO_x can be reduced to N_2 in the converter. Converters have been made of various metals, including copper and gold, and typically have efficiencies greater than 95%.

One setback to the use of the stainless steel converter is that NH_3 is also oxidized to NO, provided that oxygen is present.

$$4NH_3 + 5O_2 \xrightarrow[\text{catalyst}]{\text{heat}} 4NO + 6H_2O \qquad (26)$$

The NH_3 response has been separated from NO and NO_2 by a subtraction technique (10). A tube containing acidic $Cr_2O_7^{-2}$ on firebrick is placed in the gas stream just ahead of the entrance to the converter. The following reaction occurs: (27)

$$2NH_3 + Cr_2O_7^{-2} + 2H^+ \longrightarrow (NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$

Thus only the oxides of nitrogen are measured when the subtractive tube is used. By the difference measurement, the amount of NH_3 present in an ambient sample can be determined. The chemiluminescence method exhibits many desirable characteristics- selective response to NO and NO_2, wide range of use, accuracy and repeatability, minimal interference by common pollutants, good response time, simple sample preparation and reasonable low cost.

In the Thermoelectron Chemiluminescent Analyzer (Model 14B, the catalytic converter is molybdenum and is only sinsitive to NO_2. Thus organic nitrates such as PAN are not detected. The full scale ranges on the instrument vary from .05 to 10 ppm and the instrument can automatically cycle between measuring NO and NO + NO_2. The upper limit of detection is about 2000 ng of nitrate in a single vaporization. This can be increased by diluting the input pulse so that the detector receives a broader but lower amplitude signal. It is important that the gas entering the detector be at atmospheric pressure and in order to connect the flow to a cylinder of nitrogen, an atmospheric dump bypass is used; in that way the flow rate required by the detector is

matched exactly. The analyzer was periodically calibrated. Although calibration gases of a few tenths of a ppm in nitrogen have recently been developed by Airco Corporation, the method which we had available used a gas dilution system, as described below.

KIN-TEK PRECISION GAS CALIBRATION SYSTEM MODEL 570

Calibration of the detector requires a calibration gas consisting of no more than a few ppm NO in N_2 fed directly into the detector. The Kin-Tek is a system whereby a raw gas, in this case pure NO, is emitted into a stream of dilution gas (N_2). This is accomplished by means of a permeation membrane.

A chamber containing NO at a nominal pressure is separated from the nitrogen stream by a semipermeable membrane. The rate of flow of NO through the membrane as a function of temperature has been measured by the manufacturer. The temperature of the entire dilution chamber is held constant by a thermostat and any of three temperature set points may be chosen. The flow of nitrogen was measured with a wet test meter and was found to be 1.18 l/min at atmospheric pressure (usually 740 mm Hg).

The usual procedure was to add raw gas and wait until thermal equilibrium was reached at 30°C. All pressures were then set. The chemiluminescent analyzer monitored the concentration of the calibration gas until a constant composition was indicated. At this time the detector is set to read the proper concentration, then a second temperature set point is selected (60°C). When equilibrium is established again the difference between the observed and calculated readings was never more than .01 ppm. It usually took about 6 hours for the concentration of the calibration gas to reach a constant value. At 30°C and 60°C the concentrations of the calibration gases were .32 ppm and .71 ppm, respectively. The zero point on the detector was set prior to calibration by flowing zero air into the detector while monitoring NO. It was assumed that any NO present in the zero air would be converted into NO_2 by the O_2 so that the concentration of NO in the zero air cylinder could be taken as zero. The cylinders of nitrogen typically contained .02 ppm NO_x; this was taken into account during calibration.

All procedures were followed as per the Kin-tek instruction manual and all connections were made with teflon tubing and stainless steel Swagelok fittings.

USE OF STAINLESS STEEL CONVERTER

An attempt was made to use a different converter to obtain additional information about atmospheric composition. A stainless steel convertor heated to 750°C from a higher range chemiluminescent detector was connected in series to the 450°C molybdenum converter in our own instrument. Other investigators (10) have reported that the stainless steel converter will convert NO_2, NH_3, PAN into NO, thus allowing these species to be detected. The plan was then to use the subtractive tube to absorb NH_3 and hopefully not PAN. Then, since the molybdenum converter can only detect NO_2, one could obtain by difference the concentrations of each of the four species. Unfortunately the method did not work; two explanations are possible. One is that because the signal had been detected after a long delay it was believed that the converter was very long. The longer it was the more it tended to broaden the pulse and lower the amplitude, resulting in poorer detection. The other explanation is that since the stainless steel convertor was designed for an instrument capable of measuring 1-10,000 ppm NO_x, the converter itself may have adsorbed the NO pulse on its interior walls.

COATINGS

We studied the recovery of standards with various coatings as indicated in Table 3. It must be noted that the percent recovery with standards is not a conclusive measure of what the recovery will be from impactor samples. Whereas the impactor samples will consist of solid particles sticking to the coating, the procedure for testing with standards involves placing the aqueous standard solutions on the coating and relying on evaporation to leave the nitrate residue.

The first coating studied in the impactor was glycerol. Looking at the values in Table 4 it is seen that the coated strips do not always yield higher nitrate values. The major difficulty in using glycerol was that because it is a low viscosity liquid the air jet of

TABLE 3. BACKGROUND AND PERCENT RECOVERY FOR DIFFERENT COATINGS

COATING	BACKGROUND, ng NO_3	RECOVERY OF STANDARD, %
GLYCERIN	14	62
SILICONE GREASE	11	31
GE SILICONE OIL	10	15
MINERAL OIL	15	86
VASELINE	12	98

TABLE 4. COMPARISON OF IMPACTED NITRATE USING GLYCEROL COATED AND UNCOATED STRIPS (ALL NUMBERS $\mu g/m^3$)

	8/4/76 11:49 - 12:35			8/5/76 10:45 - 11:45			8/5/76 14:08 - 14:38		
	Coated	Stage	Uncoated	Coated	Stage	Uncoated	Coated	Stage	Uncoated
	5.94	3	4.15	6.69	3	7.04	5.11	1	3.64
5	1.67	4	1.08	1.56	4	.79	4.16	3	6.09
	.43	5	.27	.26	5	.12	.26	5	.06
	.40	6	.58	.07	6	.34	.34	6	.35
	8.44		6.08	8.58		8.29	9.87		10.14
	39% Increase			3.5% Increase			2.7% Decrease		

the impactor forced the coating toward the edges of the strip. This caused nitrate to be displaced to areas of the strip which are not heated and at the same time left the central strip area unprotected against bounce off. The vaseline coating is seen in table 5 to be consistently superior to the uncoated strip.

TABLE 5. COMPARISON OF IMPACTED NITRATE USING VASELINE COATED AND UNCOATED STRIPS (ALL NUMBERS $\mu g/m^3$)

8/10/76 11:18 - 12:00

Coated	Stage	Uncoated
3.71	1	2.33
4.99	3	5.14
2.30	5	.69
1.07	6	.46
12.07		8.62

40% Increase

8/11/76 9:28 - 10:45

Coated	Stage	Uncoated
1.46	1	.89
2.24	3	1.87
.85	4	.74
1.47	6	.33
6.04		3.83

58% Increase

8/12/76 11:28 - 13:15

Coated	Stage	Uncoated
3.24	1	1.26
4.08	2	2.16
2.76	3	1.01
2.55	4	2.84
2.78	5	1.59
2.20	6	2.97
.33	7	.47
0	8	.14
17.94		12.44

44% Increase

8/10/76 14:13 - 15:55

Coated	Stage	Uncoated
2.05	1	1.38
2.55	3	2.32
.83	5	.12
1.03	6	.18
6.46		4.00

62% Increase

APPENDIX C

Ambient Nitrate Measurements

All measurements were made during the same week under roughly the same meteorological conditions. The Hermosa Beach data were obtained from a balcony, one story above ground level (about 30 feet above sea level) at a distance of about one-quarter mile from the surf. Wind of not more than a few MPH was generally from the ocean. Pasadena measurements were made from the roof of Keck Laboratory. Measurements at Chino were made at 3 feet above ground level on the grounds of the State Correction Facility there, located adjacent to cattle feed lots.